CO adsorption and dissociation on iron oxide supported Pt particles


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We studied CO adsorption on Pt particles deposited on well-ordered Fe3O4(1 1 1) thin films grown on Pt(1 1 1) by temperature programmed desorption (TPD). A highly stepped Pt(1 1 1) surface produced by ion sputtering and annealing at 600 K was studied for comparison. Structural characterization was performed by scanning tunneling microscopy and Auger electron spectroscopy. The TPD spectra revealed that in addition to the desorption peaks at ~400 and 480 K, assigned to CO adsorbed on Pt(1 1 1) facets and low-coordination sites respectively, the Pt nanoparticles annealed at 600 K exhibit a desorption state at ~270 K. This state is assigned to initial stages of strong metal support interaction resulting in partial Fe–Pt intermixing. On both Pt/Fe3O4(1 1 1) and stepped Pt(1 1 1) surfaces CO is found to dissociate at 500 K. The results suggest that CO dissociation and carbon accumulation occur on the low-coordinated Pt sites.

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1. Introduction

Adsorption of carbon monoxide on platinum surfaces is one of the most explored reactions in surface science (e.g., see [1]). Numerous studies performed on clean Pt single crystal surfaces showed that CO preferentially occupies atop sites on Pt surfaces and also bridge sites at increasing coverage. The binding energy of CO depends on the Pt surface structure. From surfaces with low Miller indices CO desorbs in a relatively broad signal, whereas high Miller indices CO desorbs at elevated temperatures (typically, above 700 K). We have recently demonstrated that Pt particles supported on well-ordered iron oxide Fe3O4(1 1 1) films also undergo the SMSI effect via encapsulation [20,21]. Scanning tunneling microscopy (STM) studies showed that the top facets of the Pt particles annealed at temperatures above 800 K exhibit the structure of a FeO(1 1 1) film grown on Pt(1 1 1).

When supported on reducible transition metal oxides such as CeO2 and TiO2, Pt particles exhibit a so-called strong metal support interaction (SMI) [11,18,19] resulting in a dramatic decrease of CO uptake due to particles’ encapsulation by the reduced oxide support at elevated temperatures (typically, above 700 K). We have recently demonstrated that Pt particles supported on well-ordered iron oxide Fe3O4(1 1 1) films also undergo the SMI effect via encapsulation [20,21]. Scanning tunneling microscopy (STM) studies showed that the top facets of the Pt particles annealed at temperatures above 800 K exhibit the structure of a FeO(1 1 1) film grown on Pt(1 1 1).

In this work, we studied CO adsorption on Pt particles supported on Fe3O4(1 1 1) by TPD, AES, and STM. Perfect and highly stepped Pt(1 1 1) surfaces were used as reference materials. The results indicate that vacuum annealing at 600 K, i.e. before the FeO overgrowth has been observed, causes Fe migration on/into the Pt particles as the initial stage of the SMI. On both Pt/Fe3O4(1 1 1) and stepped Pt(1 1 1) surfaces CO is found to dissociate at 500 K resulting in carbon deposition. The TPD results suggest that CO dissociation and carbon accumulation occur on the low-coordinated Pt sites.
2. Experimental

The experiments were performed in two UHV chambers (TPD and STM, base pressure below $3 \times 10^{-10}$ mbar) equipped with a low energy electron diffraction/Auger electron spectroscopy setup (LEED/AES, from Specs), and a quadrupole mass-spectrometer (QMS, Hiden HAL 301). In the TPD chamber the Pt (1 1 1) crystal (~10 nm in diameter, 1.5 nm in thickness, from Mateck) was spot-welded to two parallel Ta wires used for resistive heating and also for cooling by filling a manipulator rod with liquid nitrogen. The temperature was measured by a chromel–alumel thermocouple spot-welded to the backside of the crystal.

In the STM chamber the Pt(1 1 1) crystal, mounted to a Pt sample holder, was heated by electron bombardment from the backside. The temperature was controlled using a chromel–alumel thermocouple spot-welded to the edge of the crystal. In both chambers the crystal temperature was controlled using a feedback control system (Schlichting Phys. Instrum.)

The preparation of thin Fe$_3$O$_4$(1 1 1) films on Pt(1 1 1) is described elsewhere [22,23]. Briefly, one monolayer (ML) of Fe is deposited onto clean Pt(1 1 1) at 300 K and subsequently annealed in $10^{-5}$ mbar O$_2$ at 1000 K for 2 min to form a FeO(1 1 1) monolayer film. Repeated cycles of 5 ML Fe deposition and oxidation results in Fe$_3$O$_4$(1 1 1) films as judged by LEED and STM. The average thickness of the films used in this work is about 10 nm.

Iron and Pt (both 99.95%, Goodfellow) were deposited using electron beam assisted evaporators (Focus EFM3). During deposition, the sample was biased with a retarding potential to prevent metal ions from being accelerated towards the sample. Calibration of Pt deposition rate in the TPD chamber was performed with a quartz microbalance.

3. Results and discussion

Fig. 1a and b show typical large-scale STM images of Pt/Fe$_3$O$_4$(1 1 1) surfaces that were annealed in UHV at 600 K for 5 min. The vacuum annealing was performed in order to eliminate structural changes during CO TPD experiments. At sub-monolayer coverage Pt forms two-dimensional islands, while large, well-faceted Pt particles are formed at higher coverage. Although atomic resolution was not achieved on Pt deposits (but on bare support, see [20,21]), it is conceivable that Pt particles grow on a Fe$_3$O$_4$(1 1 1) film via the same epitaxial relationships as between the film and the Pt(1 1 1) substrate underneath. The height of the particles seen in Fig. 1a is about 0.5 nm, on average, and showed almost bulk behaviour in X-ray photoelectron spectra (not shown). If the 270 K state were the metal/oxide interfacial sites, one would expect to have more of these sites at low Pt coverage where the particles are smaller and the density is higher (see Fig. 1). In fact, the Pt(1 0 0) surface exhibits a desorption peak at higher temperature than that of Pt(1 1 1). Finite size effects are unlikely, too: The particles contain hundreds of Pt atoms, on average, and showed almost bulk behaviour in X-ray photoelectron spectra (not shown). If the 270 K state were the metal/oxide interfacial sites, one would expect to have more of these sites at low Pt coverage where the particles are smaller and the density is higher (see Fig. 1). In fact, the Pt(1 0 0) surface exhibits a desorption peak at higher temperature than that of Pt(1 1 1). Finite size effects are unlikely, too: The particles contain hundreds of Pt atoms, on average, and showed almost bulk behaviour in X-ray photoelectron spectra (not shown). If the 270 K state were the metal/oxide interfacial sites, one would expect to have more of these sites at low Pt coverage where the particles are smaller and the density is higher (see Fig. 1). In fact, the Pt(1 0 0) surface exhibits a desorption peak at higher temperature than that of Pt(1 1 1). Finite size effects are unlikely, too: The particles contain hundreds of Pt atoms, on average, and showed almost bulk behaviour in X-ray photoelectron spectra (not shown).

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![STM images of the Pt/Fe$_3$O$_4$(1 1 1) surface annealed to 600 K in UHV for 5 min at 0.8 ML Pt (a) and 2.6 ML (b) Pt coverages. Image (c), presented in differentiated contrast, shows a Pt(1 1 1) single crystal surface sputtered by 1 keV Ar$^+$ ions at 300 K and then annealed to 600 K for 5 min. Image size is 100 x 100 nm; tunneling bias and current are $V_t = 1.4$ V, $I = 1$ nA (a) 1.4 V and 0.7 nA (b) 0.7 V and 0.4 nA (c).](image-url)
An O spillover onto Pt seems to be hardly possible since the affinity of Pt for oxygen is obviously lower than that of Fe. Therefore, we first address Fe migration onto Pt. To examine this hypothesis, we studied CO adsorption on 0.1 ML Fe deposited onto the stepped Pt(1 1 1) surface at 300 K and subsequently annealed in UHV at 600 K for 5 min. For this low Fe coverage one would expect Fe decorating the step edges. However, according to infrared studies [32] and Monte-Carlo simulations [33], the Fe atoms may also migrate into the sub-surface region of Pt at temperatures above 450 K. Nonetheless, Fig. 2b shows that the intensity of the high temperature peak at 510 K on the Fe/Pt(1 1 1) surface is reduced by a factor of 2, while the CO capacity of the (1 1 1) terraces is almost unchanged. Interestingly, the new CO desorption state emerges below 300 K, i.e. very similar to that observed on the Pt/Fe3O4 surface (see Fig. 2a). Weakening of the CO bond on Pt–Fe surfaces has previously been reported for the Pt-terminated Pt80Fe20(1 1 1)-(2√2) surface, where a main desorption peak is observed at 340 K [34]. The similar downshift of CO desorption by surface alloying with other metals has also been reported, e.g. on Pt–Sn [35] and Pt–Ce [36] surfaces. Therefore, the results indicate that the 270 K peak observed on the Pt particles originates from Fe migration onto the Pt particles or partial Pt–Fe intermixing upon heating to elevated temperatures.

Fig. 3 shows TPD results for CO adsorbed on 1.7 ML Pt/Fe3O4(1 1 1) at 100 K, where also the CO2 signal (44 amu) was monitored. Two CO2 desorption peaks are observed at ~150 and ~500 K, which are definitely not due to CO cracking in the mass-spectrometer. The signal at 150 K has been detected on pristine Fe3O4(1 1 1) films and thus assigned to CO2 adsorption on the oxide surface from the vacuum background upon cooling the sample to 100 K. The experiments with CO on O-precovered Pt(1 1 1) revealed CO2 formation in a broad peak between 300 and 400 K (not shown), which is missing in these spectra. Although there is some CO2 intensity at around 200 and 300 K, which could, in principle, be assigned to CO + O reaction on Pt(1 0 0) facets [31], the signal does not change upon repeating the spectra and most likely originates from the heating wires, etc. and thus can be neglected. Therefore, the results show no evidence for O spillover onto Pt particles.

The most prominent signal at ~500 K must be attributed to the reaction limited desorption of CO2 that forms on the Pt/Fe3O4(1 1 1) interface. The isotopic experiments with C18O revealed that the O atoms for this reaction come from the iron oxide film as solely the formation of C16O18O was observed on the Pt/Fe16O4(1 1 1) surface. Since CO on the (1 1 1) facets desorbs at much lower temperatures, CO2 can only be formed from CO more strongly bound to the sites that are interfacial in nature. This finding further supports the conclusion that the 270 K state cannot be assigned to the metal/oxide interface. In addition, the results show that CO on the interface sites desorbs at the same temperature (i.e. 480 K) as for other low-coordination sites such as edges and corners.

Fig. 3 shows that the CO2 production at 500 K gradually decreases in repeated CO TPD runs, indicating that oxygen reacted with CO cannot be replenished under these conditions. Interest-
ingly, the high temperature CO peak also loses intensity. In fact, the CO capacity for this state is reduced even more if one takes into account the amounts of CO that is not desorbed, but consumed to form CO$_2$. In principle, this effect could be explained by CO-induced surface restructuring (note, that the surface has been annealed for 5 min at 600 K in UHV prior to TPD studies), site blocking by carbon deposition through CO dissociation (note, however, that the above isotopic experiments showed the Boudouard reaction (2CO$^{18}$ $\rightarrow$ CO$_2$ + C) to be unfavorable), or both. The effects are expected to manifest themselves more strongly at high CO exposures.

Fig. 4a shows CO TPD spectra for 1.7 ML Pt/Fe$_3$O$_4$ pre-exposed to 1500 L CO ($\approx$10$^{-6}$ mbar, 30 min) first at 450 and then at 500 K. It is clear that CO exposure at 450 K essentially causes no change, whereas the exposure at 500 K (i) strongly reduces CO desorption from the high temperature state (i.e. 480 K); (ii) does not appreciably change CO capacity on Pt(1 1 1) terrace sites (at $\approx$400 K); and (iii) increases the signal at 100–300 K overlapping with the signal from the support. Very similar results are observed for highly stepped Pt(1 1 1) as shown in Fig. 4b. Also for the 0.1 ML Fe/ Pt(1 1 1)$_S$ surface, the CO exposure at 500 K further reduces the signal at $\approx$500 K and increases the intensity of the low-temperature shoulder due to carbon deposition (see Fig. 4c). AES analysis revealed carbon formation after experiments at 500 K (see the insets). Meanwhile, the same treatment, applied to the perfect Pt(1 1 1) surface, showed no carbon signal in Auger spectra and no changes in CO TPD (not shown).

Therefore, the results suggest that it is not the Fe–Pt intermixing within the supported Pt particles that is responsible for the CO dissociation at 500 K. In fact, the effect on Fe/ Pt(1 1 1)$_S$ is less pronounced than on the clean Pt(1 1 1)$_S$ surface (cf Fig. 4b and c), most likely due to Fe decorating the low-coordinated Pt surface atoms on which CO dissociation occurs. Indeed, both at 450 and 500 K, the (1 1 1) terraces are virtually clean in the $\approx$10$^{-6}$ mbar CO pressure used in these experiments, while CO has sufficient residence time on the low-coordination sites to dissociate before desorption. Apparently, the activation energy for CO dissociation is comparable with CO desorption energy on these sites, i.e. about 130 kJ/mol calculated using the Redhead formula [37] and a frequency pre-factor 10$^{13}$ s$^{-1}$. The carbon left by CO dissociation accumulates on the Pt low-coordinated sites and thus suppresses CO desorption from the high temperature state, i.e. at 480–500 K.

In order to determine whether CO dissociation depends on the Pt particle size, the experiments were performed for different Pt coverages as shown in Fig. 5. For all samples, high CO exposure at 500 K resulted in carbon deposition as shown in the AES spectra presented in the insets. Concomitantly, the 480 K peak is strongly reduced, in particular for the highest Pt coverage studied, while a broad desorption signal at temperatures below 300 K gains intensity and overlaps with the signal of the bare support. (Note that the same exposure to pure Fe$_3$O$_4$(1 1 1) films did not result in new CO desorption states and carbon deposition).

The carbon deposits can be removed by reaction with 10$^{-6}$ mbar O$_2$ at 500 K. The chemisorbed oxygen left on the Pt surface is in turn removed by CO at 450 K, i.e. at the temperature when no CO dissociation occurs (see Fig. 4). This procedure is similar to that previously used for the Pd/Al$_2$O$_3$/NiAl(110) system [38,39], and practically recovers the original CO TPD spectra and cleanliness of the Pt surfaces as judged by AES.

The results, presented in Figs. 4 and 5, show that the CO capacity for the (1 1 1) terrace sites is least affected by carbon deposition (as more clearly observed on the stepped Pt(1 1 1) surface). Therefore, it is plausible that carbon blocks the low-coordinated Pt sites and thus weakens CO bonding to the adjacent terrace sites, ultimately resulting in the low-temperature desorp-
4. Conclusions

Comparative STM, AES and CO TPD study of Pt/Fe₃O₄(1 1 1), perfect Pt(1 1 1) and highly stepped Pt(1 1 1) surfaces showed that the Pt nanoparticles annealed at 600 K exhibit a new desorption state at ~270 K. This state is assigned to initial stages of strong metal support interaction resulting in Fe migration onto the Pt particles, although Fe diffusion into the particles at these temperatures cannot be excluded.

Both on Pt/Fe₃O₄(1 1 1) and stepped Pt(1 1 1) surfaces CO is found to dissociate at 500 K resulting in deposition of carbon, supporting the previous literature results on the key role of low-coordinated sites in CO dissociation on Pt. The results also suggest that carbon accumulation occurs on the low-coordinated Pt sites. Carbon deposits can be removed by mild oxidation at 500 K.

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References